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**Impact of nutrients supply and pH changes on the elimination of hydrogen sulfide,
dimethyl disulfide and ethanethiol by biofiltration**

Mouna Ben Jaber^{1,2}, Benoît Anet³, Abdeltif Amrane^{*1,2}, Catherine Couriol^{1,2}, Thomas Lendormi⁴, Pierre Le Cloirec^{1,2}, Gilles Cogny⁵ and Romain Fillières³

1. Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes 1, CNRS, UMR 6226, Avenue du général Leclerc, CS 50837, 35708 Rennes Cedex 7, France

2. Université européenne de Bretagne, 5 Boulevard Laënnec 35000 Rennes France.

3. Akiolis Group, 72 Avenue Olivier Messiaen, 72000 Le Mans, France

4. Laboratoire d'Ingénierie des Matériaux de Bretagne, EA 4250, Université de Bretagne Sud, Allée des Pommiers, 56300 Pontivy, France

5. Atemax France, Route d'Alençon, 61400 Saint-Langis-lès-Mortagne, France

*Corresponding author. Tel:+33 2 23 23 81 55; Fax : + 33 2 23 23 81 20

E-mail address: abdeltif.amrane@univ-rennes1.fr

Abstract

The treatment of sulfur odorous compounds in mixture, Hydrogen sulfide (H_2S), dimethyl disulfide (DMDS) and ethanethiol (EtSH), by biofiltration was examined. A significant effort was focused on the impact of nutrients supply, without forgetting the effect of other parameters such as the pH, on the process performances. Removal efficiencies of three biofilters packed with pine bark and composted wood mulch and sprinkled by different nutritive solutions were compared.

Owing to the biodegradability of H_2S , its removal was not affected by the lack of nutrients in the biofilter. However, for EtSH and DMDS, considered as more recalcitrant, the influence of nutrients on biodegradation was clearly observed; it was enhanced when the supplementation in the watering solution was increased. Furthermore, EtSH removal yield increased from 80% in the absence of supplementation to an almost total removal in the presence of nutrients in the watering solution. The degradation of the three compounds decreased as follows: $H_2S > DMDS > EtSH$. The impact of the pH of the packing materials was also underlined. The decrease in pH caused by the accumulation of sulfuric acid in the packing material, the most abundant product of the biological oxidation of sulfur compounds, led to a reduction of the elimination efficiencies of EtSH and DMDS; while the microorganisms involved in H_2S degradation appeared active in a large pH range, from less than 3 to close to 9.

Keywords: Biofiltration; Sulfur compounds; Nutrients; pH; Elimination efficiency.

1. Introduction

Odor nuisances related to industrialization is an emerging problem attracting the attention of public authorities who implement an increasingly strict regulation concerning odor emissions [1]. Perception thresholds of pollutants, especially those of sulfur compounds,

which are very low, force to achieve high abatement rates; otherwise the residual concentrations may cause significant impacts on the welfare of local populations [2-4].

Various technologies are available for the treatment of these gaseous emissions; among them biological processes show some favorable advantages, since they are especially suitable for high gaseous flow rates (in the order of a hundred thousand of cubic meter of air per hour) containing low pollutant concentrations (below one gram per cubic meter) [5] [6,7]. In addition, biological processes in general and biofiltration in particular, show limited costs and an ease of use justifying their use for the deodorization of industrial emissions [8-11].

A biofilter consists of a porous organic or inorganic bed, through which passes a humid polluted gaseous stream. In a biofilter, the contaminants are absorbed from the gas phase to the biofilm, consisting of a thin layer of water and microorganisms, where the biological reactions occur [12]. Pollutant transfer and biodegradation kinetics rely on material characteristics such as: pH, water holding capacity, organic matter and nutrients content, and structural behaviour [8,13]. Biofiltration is therefore a complex process, involving various phenomena, such as mass transfer, adsorption, absorption and microbial activity [14]; they are closely linked to the biofilm and hence the packing material [15], which represents therefore the cornerstone of the process [13,16]. Intrinsic packing material's properties induce the establishment of a more or less conducive environment for the development of an effective microbial consortium and homogeneous gas distribution through the bed.

For this purpose, the chemical, physical and microbial properties, as well as the economical impact, of 11 organic and inorganic packing materials potentially suitable for biofiltration have been previously investigated in order to select the most relevant for the treatment of rendering gaseous emissions.. Among them and according to its appropriate pH, water holding capacity and its highest nutrients content and colonization at the biofilter start up, composted

would mulch showed the best odour removal efficiency. However, the pressure drop of the compost bed decreased suggesting structural changes which may impact the performances on long term. On the contrary, pine bark showed almost constant height and pressure drop during the operation time suggesting that its structure remained stable over time, while its performances remained significant [17]. In addition, the use of pine bark has been recommended by other authors in odor treatment [18], while total H₂S removal was observed in a biofilter containing compost-based bed [19].

Therefore, the packing material considered in the present work was constituted of a stratum of pine bark covered by a stratum of composted wood mulch to combine the physico-chemical benefits of the former and the efficiency of the latter. The packing medium should contain nutrients in a sufficient amount to allow microbial activity; however it is not always the case. Consequently, the impact of nutrients supply on treatment performance was examined.

Most of the laboratory studies focus on the treatment of gaseous effluent containing only one pollutant; while industrial effluents usually contain a complex mixture of pollutants, and hence removal efficiency differs significantly from that observed in the case of a single pollutant [20-23]. Removal capacities of biofilters differ according to the considered pollutant and biodegradability decreases as follows: alcohols > esters > ketones > aromatic compounds > sulfur compounds, showing the recalcitrance of sulfur compounds [2,24], which have been therefore selected for this study. They also show very low perception thresholds associated with high olfactory contributions [2] and can be nearly always found in industrial emissions.

Among sulfur compounds, biodegradability decreases as follows: H₂S > methyl mercaptan > dimethyldisulfur (DMDS) > dimethylsulfur (DMS) [25], and total H₂S removal was usually the case [26,27]. Among them, H₂S and DMDS were selected for this study, as well as ethyl mercaptan (EtSH) which is also often reported in gaseous emissions.

Biological oxidation was realized by sulfato-oxidative bacteria, leading to H_2SO_4 and CO_2 [28] and hence affecting significantly the pH, which has been therefore monitored during the course of the experiments.

2. Materials and methods

2.1. Experimental Set Up

The biofiltration unit consisted of three identical PVC columns with an internal diameter of 150.4 mm. For clarity reasons, only one column is shown in Figure 1.

Each column was composed of two stratum: a 50 cm pine bark layer chosen for its good physical proprieties supports, a 50 cm composted wood mulch stratum selected according to its propensity to bring diversified microbial communities and its low cost.

The compressed air was humidified at room temperature and fed in the bottom of the biofilter using a bubbler thus achieving a relative humidity close to 99%.

The reserve of liquid pollutants (DMDS and EtSH supplied by Acros Organics with respective purity of 98 and 99%), supplying the two mass regulators disposed in series, was a 250 mL steel 316 Swagelok cylinder pressurized under 2 bar of compressed air. The operating principle was based on the evaporation of a liquid, diluted in a carrier gas stream. Rates of these two streams were respectively controlled by regulators μ -FLOW mass liquid and gaseous EL-FLOW (Bronkhorst ®, Montigny-Les-Cormeilles, France). The volatilization chamber was flushed by a controlled flow rate of a compressed air stream supplied under 5 bars (Bronkhorst ®, Montigny-Les-Cormeilles, France). High concentrated flow of hydrogen sulfide was provided to the system by a gas tank concentrated at 2500 ppm in nitrogen (Linde Gas France S.A., Noyal sur Vilaine, France). The feed rate of each column was measured by a flowmeter stainless steel ball (Brooks® GT1355, Hatfield, PA, USA).

Biofilter watering was ensured by a peristaltic pump for selecting a nutrient solution or deionized water at neutral pH and at a flow rate of 0.344 L day^{-1} . The dispersion was carried on by stainless steel full cone nozzle GG-SS1 FullJet supplied by Spraying Systems Emani® (130 ml min^{-1} , spray angle: 60° , at 0.5 bar) (Arcueil, France). This solution was used to maintain the growth of microorganisms in the packing material in order to improve pollutant removal in the biofilter.

Two pH measuring points were located respectively at 25 and 75 cm from the biofilter bottom. Eight points for gas sampling, separated by 12.5 cm each, were distributed over the entire height of each column.

2.2. The packing material

The characterization of packing materials properties was realized according to standards methods [17,29]; these characteristics are reported in Table 1.

The used pine barks were a mixture of black pines and maritime pines and supplied by Hobiofilter S.A.R.L. (Mazères, France). The composted wood mulch was supplied by Europe Environnement (Aspach Le Haut, France).

2.3. Inoculation

At the biofilter start-up, the three different columns were inoculated with 500 mL of diluted activated sludge (initial dry weight 1.2 g L^{-1}) recovered from wastewater treatment plant (Beaurade, Rennes, France).

2.4. Analytical methods

Inlet and outlet H_2S , EtSH and DMDS concentrations were measured by a TRS MEDOR® analyzer (Chromatotec, France). The separation was performed on a capillary column swept by reconstituted air under 230 mbar, followed by an electrochemical detection in a cell filled with CrO_3 at 10 g L^{-1} . Samples of 400 μL of gas were used for the measurements. The retention times were 70, 110 and 290 s for dimethyl disulfide (DMDS), hydrogen sulfide

(H₂S) and ethanethiol (EtSH), respectively. The detection limits ranged between 35 and 45 µg m⁻³ for these pollutants. The external calibration was managed with a mixture containing 20 mg m⁻³ (± 2 mg m⁻³) for each component supplied by Linde Gas France S.A. (Noyal sur Vilaine, France) and internal calibration was managed by a dimethylsulfide permeation furnace (107.4 ng min⁻¹ at 45°C).

The pH of the leachates and in the packing materials was measured using a CyberScan pH510. In order to limit the gaseous distribution through the packing, the pH was measured with a penetration probe (Mettler Toledo, Greifensee, Switzerland).

2.5. Operating conditions and start-up

A 3.2 m³ h⁻¹ flow rate was applied leading to 60 s empty bed retention time (EBRT). During this study, an increase in pollutant concentrations was applied in order to compare the removal efficiencies of the three biofilters and to follow the influence of nutrients supply facing concentrations increase. The operating conditions are reported in Table 2. It should be observed that the considered pollutant concentrations were selected according to the range of values reported in the literature [2,31-33].

Nutrients were supplied by a nutritive solution dispersed on the surface of the biofilter. In order to follow the impact of nutrients supply on the degradation of a mixture of pollutants, the three columns were watered by different solutions with a fixed rate of 0.344 L day⁻¹. The first biofilter (BIO1) operated without nutrient supply; it was just sprinkled by deionized water. Different nutritive solutions were supplied to the second (BIO2) and third (BIO3) biofilters. The composition of these solutions is shown in Table 3. Na₂CO₃ was added to supply for inorganic carbon since regarding sulfur compounds, even if both autotrophic [34] and heterotrophic [35,36] pathways can be considered, the autotrophic pathway is the most often reported in the available literature [34,37]; while composted wood mulch was expected

to supply for organic carbon. Regarding K_2HPO_4 and $(NH_4)_2SO_4$ they were added to supply for nitrogen, phosphate and sulfate for microbial growth.

The removal efficiency RE of each bed was calculated as follows:

$$RE (\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100$$

Where RE: removal efficiency (%); C_{in} : inlet concentration ($mg\ m^{-3}$); C_{out} : outlet concentration ($mg\ m^{-3}$).

3. Results and Discussion

3.1. Influence of nutrients supply on treatment performance

During the first phase (until 14 days), it was observed that H_2S was totally eliminated from the first day (Fig.2a), showing that nutrients supply had no influence on the abatement of H_2S in the considered conditions. Contrarily and even at low pollutants concentration (first phase), about 3 and 5 days were needed to achieve total EtSH and DMDS removal (Figs.2c and b). The negligible impact of nitrogen and phosphorus addition on H_2S removal should be most likely related to their presence in the organic packing material used, composted wood mulch and pine bark. In addition, it was shown that in the presence of a mixture of sulfur compounds, H_2S is preferentially metabolized [26,38].

An increase of the pollutant concentrations ($7.6\ mg\ m^{-3}$ – phase 2 – from day 14 to day 79) clearly highlighted the influence of nutrients supply on the degradation of EtSH and DMDS. Indeed, the removal efficiencies of these compounds in the columns sprinkled by nutrient solutions (BIO2 and BIO3) were higher than those in the first biofilter operating just with deionized water. The positive impact of nutrients appeared however limited in the case of DMDS, while it was especially pronounced in the case of EtSH. Indeed, final removal

efficiencies were 95 and 82% for DMDS and EtSH in the absence of nutrients (BIO1) (Figs.2b and c), while total DMDS removal (Fig.2b) and 95% EtSH removal (Fig.2c) were observed for a low supplementation (BIO2) and total removal of both pollutants for the high supplementation (BIO3) (Figs.2b and c). Therefore and in most cases, the presence of nutrients is required to improve the biodegradation of recalcitrant sulfur compounds, in agreement with the available literature showing that nutrient deficiency may become a limiting factor for biofiltration efficiency [39]. These results clearly showed that microorganisms consumed preferentially the most easily biodegradable compound (H_2S) in the biofilter to the detriment of the most recalcitrant pollutants (DMDS and EtSH). When treating a mixture of sulfur compounds, the presence of H_2S inhibits the removal of some organic reduced compounds (EtSH and DMDS) which are more recalcitrant to biodegradation [27].

From these results, an order of degradation of these compounds can be established as follows:
 $H_2S > DMDS > EtSH$.

It should be observed that analysis of the impact of nutrients addition can only be qualitative but not quantitative owing on the one hand to the involvement of the packing material, and especially composted wood mulch, in the supply of nutrients, and on the other hand to the pathway involved in organic sulphur compounds assimilation, such as EtSH and DMDS, which can be both autotrophic [34] and heterotrophic [35,36].

To examine system stability and reliability, experiments were ceased for two weeks (Fig.2). A clear impact on DMDS and EtSH removals was shown, while it appeared negligible on H_2S elimination, since no decrease of its removal yield can be observed (Fig.2a). Regarding DMDS, even if a decrease was noted after cessation of operation, the abatement rapidly

increased again until recovering stable removal efficiencies, close to those observed before cessation of operation (Fig.2b). Contrarily, a more significant impact on EtSH abatement can be noted, since an important lapse of time was needed (until approximately day 70) before recovering removal efficiencies observed before cessation of operation (Fig.2c).

3.2. Influence of pH on the removal of H₂S, DMDS and EtSH

The pH has a significant impact on treatment efficiency; microbial activity and colonization is disturbed by any modification of pH in the biofilter [40,41]. The pH was therefore monitored in the middle of each stratum, namely at 25 and 75 cm height, and showed a decrease in the two stratus (Figure 3). At the end of experiment, in all biofilters the pH was lower than 6.5 in the stratum of composted wood mulch and less than 3 in the stratum of pine bark. From this, the nutrient solution or water added to biofilter can maintain pH on the top of the bed, while the decrease was more pronounced at the bottom, from about 7 to less than 3, versus from about 8.5 to 6.5 at the top.

It should however be observed the similar pH time-courses observed for the three biofilters, close pH in all biofilters can be noted for a given time (Fig.3). The impact of the nutrients solution on the pH appeared therefore negligible.

In addition, at the beginning of the experiments, the pH of the aqueous phase collected at the bottom of each column was neutral. Over time these leachates became acidic (Fig.4); from the 10th day, the pH was less than 6 and decreased until final values close to 2.2 (Fig.4).

Both autotrophic [34] and heterotrophic [35,36] pathways can be considered for the assimilation of organic sulphur compounds, such as EtSH and DMDS. However, the autotrophic pathway, as it was also the case for H₂S assimilation, is the most often reported in the available literature [34,37]. Sulfur compounds assimilation as energy sources leads to the production of H₂SO₄ inducing medium acidification [42], as experimentally confirmed since

the amount of sulfates accumulated in the leachate at the end of the first running period was close to 1 g. H_2S removal was not affected by pH; it was completely removed in the biofilter. Regarding EtSH and DMDS and even if their removal was reported to be optimal when the pH of the bed remains between 6 and 8 [43], biofilter acidification with time did not seem to have an impact on their assimilation, since and even after a disturbance phenomenon (cessation of operation) optimal removal efficiencies were recovered.

3.3. Removal of H_2S , DMDS and EtSH along the biofilter

The elimination of H_2S , EtSH and DMDS was followed all along the biofilters height. Removal efficiencies values at days 3 and 72, namely for the low and high pollutant amounts are given in Figs.5 and 6 for instance. In addition, the mean pH values in the stratum of pine bark and that of composted wood mulch are given in Table 4.

As indicated above (see 3.2), the degradation of H_2S was not affected by the pH of the packing materials; microorganisms involved in H_2S degradation can tolerate acidic conditions [44]. For the low pollutant concentrations, the influence of nutrients supply appeared also almost negligible since no real difference between the three biofilters can be underlined (Fig.5a). The total bed height was not needed for a complete H_2S removal, since it was totally eliminated on 87.5 cm height irrespective of the considered biofilter.

About half of the H_2S was removed in the pine bark (first 50 cm), namely in the most acidic part of the bed (mean pH of 6.63 – Table 4) and the rest was removed in the composted wood mulch, namely at alkaline pH (mean pH of 8.54 – Table 4).

Contrarily to H_2S , EtSH and DMDS removals were clearly affected by nutrients supply in the aqueous solution, and this impact was especially pronounced in the case of a total absence of nutrients in the spraying water (Figs.5b and c). Only about 30% of EtSH and DMDS were removed in the first part of the bed, pine bark, and only 63 and 72% of DMDS and EtSH on

the total bed height in the absence of nutrients supply, respectively; while in the presence of nutrients in the watering solution removal yields were in the range 90-97% (Figs.5b and c).

During the second phase, namely at high pollutant concentrations, possible pH impact on the removal efficiencies can be more clearly highlighted, since medium acidification continued and from the 65th day pH below 3 were measured in the three columns in the first stratum of the bed, pine bark. As observed, H₂S removal was not affected by the pH, since even in the absence of nutrients supply only 62.5 cm of the bed were needed for its complete elimination and about 82% was removed in the pine bark (Fig.6a), where the mean pH was 2.9 (Table 4).

Microbial populations involved in H₂S degradation appeared therefore active in a large pH range, from less than 3 in the pine bark at the end of the second phase to close to 9 in the composted wood mulch in the beginning of the first phase (Table 4).

The impact of nutrients supply on the one hand and that of pH on the other hand were clearly shown regarding the degradation of the other sulfur compounds, DMDS and EtSH. Indeed, their degradation in the pine bark remained limited, since DMDS and EtSH removal efficiencies in the stratum of pine bark were 10 and 15% in the absence of nutrients supply, 10 and 15% for the low supplementation, and 40 and 25% for the high supplementation (Figs.6b and c). Regarding biofiltration at high pollutant amounts (BIO3), it should be observed that less than 20% pollutants degradation were obtained on the first 40 cm of pine bark (Figs.6b and c). The main part of DMDS and EtSH was therefore removed in the second stratum, composted wood mulch, namely at neutral pH (mean pH close to 6 – Table 4), since an almost total DMDS removal was observed in all biofilters (Fig.6b) and an almost total EtSH removal in BIO2 and BIO3 (Fig.6c). The pH impact was therefore clearly shown; DMDS and EtSH removal occurred mainly at neutral pH in agreement with the relevant literature [45].

The impact of nutrients supply was also clearly underlined, and appeared significant for the three pollutants. Indeed, pine bark was almost enough for a total H₂S degradation for the high

supplementation (Fig.6a), while about 62 cm of bed was needed for its total removal during the other experiments (BIO1 and BIO2 – Fig.6a). An improvement of the DMDS and EtSH degradation rates were also shown at high supplementation (Figs.6b and c); while a total absence of nutrients had also an impact on the rate of EtSH degradation, as well as on its final removal yield, less than 80% versus about 95% for the other experiments, BIO2 and BIO3 (Fig.6c).

4. Conclusions

The obtained results showed a significant impact of nutrients supply and pH on sulfur compounds biodegradation. An improvement of the DMDS and EtSH degradation rates were shown at high nutrients supply; while a total absence of nutrients had an impact on both the rate of EtSH degradation, and its final removal yield, less than 80% versus an almost total removal for the other experiments. Nitrogen and/or phosphorus limitations should be most likely considered to account for this nutrients effect; this assumption should be subsequently validated. An effect of the nutrients addition was also shown for H₂S at high supplementation, even if it was always totally removed.

Microbial populations involved in H₂S degradation appeared to be active in a large pH range, from less than 3 to close to 9; while and in agreement with the relevant literature, DMDS and EtSH removal occurred mainly at neutral pH. As expected, the most easily biodegradable compound (H₂S) was preferentially consumed to the detriment of the most recalcitrant pollutants (DMDS and EtSH).

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Table 1. Characteristics of the packing materials used.

Properties	Composted wood mulch	Pine bark
pH	8.62	4.75
%C	36.6%	48.1%
%O	25.5%	45.4%
%H	3.5%	5.9%
%N	1.1%	0.1%
ε (-) ^a	45.5%	56.3%
ρ (kg m ⁻³) ^b	254	213
C_{H_2O} (g g ⁻¹) ^c	1.4	2.4

^aVoid fraction; ^bDensity; ^cWater holding capacity

Table 2. Operating conditions in the three biofilters during the two experimental phases

Phas	Duration	[H ₂ S]	[EtSH]	[DMDS]	Q _{gas}
e	(days)	(mg m ⁻³)	(mg m ⁻³)	(mg m ⁻³)	(m ³ h ⁻¹)
1	14	3.8	3.8	3.8	3.2
2	65	7.6	7.6	7.6	3.2

Table 3. Composition of the spraying solution in the three biofilters

Bi	B	BIO2	BIO3
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of I			
lte O			
r 1			
		[K ₂ H	[K ₂ H
N	d	PO ₄]	PO ₄]
utr	e	= 0.02	= 0.12
ie	i	$\frac{\text{g L}^{-1}}{[(\text{NH}_4$	$\frac{\text{g L}^{-1}}{[(\text{NH}_4$
nt	o) ₂ SO ₄]) ₂ SO ₄]
s	n	= 0.08	= 0.48
so	i	$\frac{\text{g L}^{-1}}{[\text{Na}_2\text{C}$	$\frac{\text{g L}^{-1}}{[\text{Na}_2\text{C}$
lut	z	O ₃]=	O ₃]=
io	e	0.39 g	1.97 g
n	d	w L ⁻¹	L ⁻¹
		a	
		t	
		e	
		r	

Table 4. Mean pH values for pine bark and composted wood mulch on the 3rd and the 72nd days

pH					
pine bark			composted		
			wood mulch		
Biofilt	Day	3	72	3	72
er					

BIO1	6.52	2.92	8.44	5.92
BIO2	6.6	2.87	8.51	6.05
BIO3	6.76	2.71	8.68	6.6

Figure legends

Figure 1. Schematic representation of the experimental setup: *1* air inlet, *2* humidifier, *3* reserve of liquid pollutants (DMDS+EtSH), *4* volatilization chamber, *5* H₂S gas cylinder, *6* flow meter, *7* water or nutrient solution reservoir, *8* pump, *9-11* pH measuring points, *12-18* points of gas sampling, *19* leachate outlet.

Figure 2. Elimination efficiency (%) of H₂S (a), DMDS (b) and EtSH (c) in the three biofilters.

Figure 3. pH time-courses in the three biofilters in the middle of the first and second stratum, 25 and 75 cm bed height respectively.

Figure 4. pH time-courses in the leachates of the three biofilters.

Figure 5. Removal of H₂S (a), DMDS (b) and EtSH (c) along the biofilter height (on the 3rd day).

Figure 6. Removal of H₂S (a), DMDS (b) and EtSH (c) along the biofilter height (on the 72nd day).